

Synthesis and Surface-Active Properties of a Trisiloxane-Modified Oligo(propylene oxide-*block*-ethylene oxide) Wetting Agent

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ABSTRACT: Polydisperse 1,1,1,3,5,5,5-heptamethyltrisiloxane-oligo(propylene oxide-*block*-ethylene oxide) wetting agents were synthesized through the hydrosilylation of 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) with active hydrogen and allyl oligo(propylene oxide-*block*-ethylene oxide) [allyl oligo(PO-*b*-EO)] with hexachloro dihydrogen platinate(IV) as a catalyst. Allyl oligo(PO-*b*-EO) with a hydrophilic-hydrophobic balance was synthesized through the combination of propylene oxide (PO) and ethylene oxide with allyl alcohol. The wetting agents with a hydrophilic-hydrophobic balance were synthesized. The aqueous solutions of the wetting agents (0.1 wt %) were almost visibly turbid. An increase in the number of hydrophobic groups of HMTS and PO for the wetting agents resulted in a lower

critical solution temperature. Lower surface tensions of 20–25 dyn/cm were found above the critical micelle concentration (cmc), and they decreased with an increase in the number of hydrophobic groups. The cmc's were below 0.01 wt %, decreasing with as the number of hydrophobic groups increased. The wetting power and emulsion stability for the oil-in-water systems increased as the concentration of the wetting agents increased, and they decreased as the number of hydrophobic groups increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3292–3302, 2004

Key words: hydrosilylation; surface tension; critical micelle concentration; wetting power; emulsion stability

INTRODUCTION

Silicone is highly surface-active in both aqueous and nonaqueous media, lowering surface tensions to nearly 20–25 dyn/cm. It is used in a wide range of applications requiring unique properties, including polyurethane foam, textile, and fiber manufacturing, personal care products, paints and coatings, and wetting agents for textiles and fibers.

Aqueous solutions of trisiloxane wetting agents on hydrophobic solid surfaces (water contact angle > 90°) rapidly become wet and significantly reduce surface tensions. This phenomenon of wetting and spreading frequently occurs in many industrial applications.^{1–6} The spreading of siloxane wetting agent (or superspreader) solutions significantly exceeds expectations for liquid diffusion.¹ Nikolov and others^{1,7–9} suggested that this rapid spreading on a hydrophobic solid surface could be understood as a Marangoni flow-driven process. The spreading establishes a dy-

namic surface tension gradient. The driving force for the spreading is the Marangoni effect; that is, the higher the gradient is, the faster the spreading is. Moreover, the spreading is influenced by the interfacial energy of the liquid/gas, solid/liquid, and gas/liquid, as shown by molecular dynamics modeling. However, this phenomenon is not well understood.¹ In addition, the aggregates and vesicles formed in a siloxane wetting agent solution do not initiate the spreading process. Therefore, these structures are not a requirement for the spreading process.^{10,11}

To study the superspreading of siloxane wetting agents, Nikolov et al.¹ observed the drop shape and dynamic contact angle during the early stages. The spread rate reaches its peak and remains constant during this period. The droplet covers 60–70% of the final spread area during this first stage of spreading. The drop size also has no significant effect on the rate of spreading, which decreases as the surfactant concentration increases beyond the optimum surfactant level. Therefore, it is understood that surface spreading occurs beyond a certain surfactant concentration.

Wagner and coworkers^{2–6} discussed how the ethylene oxide (EO) chain length depended on the surface spreading behavior of siloxane wetting agents. They observed the synthesis of a single component of the polydisperse superspreader Silwet L77 (a polydisperse triethylene-to-dodecaethylene glycol hydrophile

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TABLE I
Notation and Recipes for Allyl Oligo(PO-*b*-EO)

Notation	AlOH (mol)	Additive unit		KOH (mmol)	$M_{n,theo}$
		PO (mol)	EO (mol)		
A04	1	—	4	5.2	234.29
A05	1	—	5	5.2	278.34
A06	1	—	6	5.2	322.40
A07	1	—	7	5.2	366.45
A16	1	1	6	5.2	380.48
A25	1	2	5	5.2	394.50
A34	1	3	4	5.2	408.53

$M_{n,theo}$ = theoretical number-average molecular weight.

attached to the trisiloxane moiety via a short trimethylene spacer) and the difference between the single-component derivatives and Silwet L77. The water solubility increased as the oligoethylene glycol chain length increased. The hexaethylene glycol derivative occupied the largest spreading areas and showed the highest initial spreading velocities. Likewise, polydisperse Silwet L77 spread more quickly than the single components. It was also nearly independent of the temperature and the phase state of the solution.

Siloxane wetting agents dissolved in aqueous solutions become hydrolyzed SiO₂ and silicone oils over time. As hydrophilic groups incorporated into non-ionic silicone surfactants are linear, or the end capping of hydrophilic groups is hydroxy, the surface tension of aqueous solutions increase because of the hydrolysis of the siloxane backbone. Therefore, linear siloxane wetting agents are relatively easily hydrolyzed. However, their resistance to hydrolysis can be improved by the introduction of a graft type, which is less sensitive to hydrolysis than a linear type. Consequently, siloxane wetting agents are prepared by the grafting of siloxane backbones and hydrophilic copolymers.^{12,13}

The advantage of grafted copolymers is that they are more resistant to hydrolysis and chemical attack than linear types. A major class includes poly(dimethylsiloxane)s to which polyethers are grafted through a hydrosilylation reaction. This process results in alkyl-pendant copolymers, in which the poly(alkyl oxide) groups are attached along the siloxane backbone through a series of hydrolytically stable —Si—C— bonds. Another class includes poly(dimethylsiloxane)s to which polyethers are attached through condensation chemistry. This creates an alkoxy-end-blocked copolymer, in which the poly(alkylene oxide) groups are attached at the ends of the siloxane backbone through —Si—O—C— bonds. This linkage offers limited resistance to hydrolysis under neutral or slightly base conditions, but it breaks down under strong acid or base conditions.^{12,13}

Therefore, in this study we synthesized various 1,1,1,3,5,5,5-heptamethyltrisiloxane-oligo(propylene

oxide-*block*-ethylene oxide) [HMSTS-oligo(PO-*b*-EO)] samples to investigate the chain-length effect of a hydrophilic group on the surface-active properties of polydisperse siloxane wetting agents. Polydisperse allyl oligo(propylene oxide-*block*-ethylene oxide) [allyl oligo(PO-*b*-EO)]¹⁴ with allyl end groups was synthesized through an addition reaction. HMSTS-oligo(PO-*b*-EO) was obtained through the hydrosilylation of the derivatives and 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMSTS) with active hydrogen. The surface-active properties, such as the surface tension, wetting power, and emulsion stability, of the HMSTS-oligo(PO-*b*-EO) wetting agents with respect to the chain length, as well as the hydrophilic–hydrophobic ratio of oligo(propylene oxide-*block*-ethylene oxide) [oligo(PO-*b*-EO)], were studied.

EXPERIMENTAL

Materials

HMSTS (Aldrich, Milwaukee, WI) and hexachloro dihydrogen platinate(VI) (CPA; Aldrich) were used without further purification. The synthesis of allyl oligo(PO-*b*-EO) was induced through the combination of EO and propylene oxide (PO), with allyl alcoholate as a catalyst (Table I). Isopropyl alcohol (IPA; Samchun Chemical Co., Korea) was used after distillation with CaH₂.

Synthesis of HMSTS-oligo(PO-*b*-EO)

For the synthesis of HMSTS-oligo(PO-*b*-EO), HMSTS, allyl oligo(PO-*b*-EO), IPA, and CPA were placed in a 300-mL, four-necked round flask fitted with a stirrer, a thermocouple, a nitrogen inlet, and a condenser (Table II). The reaction mixture was stirred under nitrogen for 30 min at room temperature and then under nitrogen at 85°C for the removal of moisture and oxygen.

TABLE II
Notation and Recipes for HMSTS-oligo(PO-*b*-EO)

Notation ^a	Allyl oligo (PO- <i>b</i> -EO)		HMSTS (mol)	Pt (mmol) ^c	$M_{n,theo}$
	Type ^b	(moles)			
H04	A04	1	1	0.1	456.79
H05	A05	1	1	0.1	500.84
H06	A06	1	1	0.1	544.89
H07	A07	1	1	0.1	588.94
H16	A16	1	1	0.1	602.97
H25	A25	1	1	0.1	617.08
H34	A34	1	1	0.1	631.03

$M_{n,theo}$ = theoretical number-average molecular weight.

^a 20 wt % solid content; solution reaction of isopropyl alcohol.

^b Poly(propylene oxide-*b*-ethylene oxide) allyl ether.

^c Pt catalyst (CPA).

The end point of the reaction was determined from Fourier transform infrared (FTIR) monitoring of an Si—H bond of HMTS and a C=C bond of allyl oligo(PO-*b*-EO). After the reaction, the reaction mixture was placed *in vacuo* at 60°C for evaporation and was subsequently filtered for precipitated black particles.

Measurements

FTIR spectra were recorded with a Biorad FTS-7 spectrometer (USA), and the ¹H-NMR spectroscopy of the reactants and products dissolved in CDCl₃ was recorded at the ambient temperature with a Varian Mercury 300 model (Palo Alto, CA). The chemical shifts were reported as parts per million downfield from tetramethylsilane. Gel permeation chromatography (GPC) analyses (Waters Co., Milford, MA) were conducted in tetrahydrofuran on a Waters Styragel HR4 column with a refractive-index detector at 35°C. The flow rate was 1.0 mL/min. Polystyrene standards were used for the molecular weight calibration. Thermogravimetric analysis (TGA; TGA-50, Shimadzu, Kyoto, Japan) was carried out from room temperature of up to 600°C at a heating rate of 20°C/min under a nitrogen atmosphere.

The phase-transition temperature (T_p) of HMTS-oligo(PO-*b*-EO) through hydrosilylation was determined with a thermo-optical analysis (TOA) instrument equipped with a Mettler FP82HT hot stage (USA), a Mettler FP 90 central processor, and an Olympus BX50 optical polarized microscope (USA).¹⁵ Aqueous solutions of the wetting agents (1.0 wt %) were prepared and stored at 30°C for 24 h. These solutions were injected into a 50-mm-long capillary tube, with a 3-mm inner diameter, that was sealed on both sides. After these tubes were sonicated for 5 min for the removal of foam, TOA was performed from room temperature up to 150°C at a heating rate of 5.0°C/min in nitrogen. T_p was assumed to be the midpoint of the T_p region in the TOA thermograms.

The surface tension was measured with Shimadzu Du Nouy surface and interfacial tensiometer, with a platinum ring 20 mm in diameter. Aqueous solutions of the wetting agents synthesized through hydrosilylation were prepared in various concentrations of 0.001–0.1 wt %, sonicated for 5 min for the removal of the foam in the solutions, and subsequently stored at room temperature for 24 h. The surface tension was assumed to be an average value measured at various times. It was analyzed from plots of the surface tension of the solutions against the logarithm of the surfactant concentration (Gibbs plots). The critical micelle concentrations (cmc's) of wetting agents were determined by the analysis of the intersection point of the plateau region and the steeply downward sloping portion of the plots determined through extrapolation.^{16–21}

For the measurement of the wetting power, aqueous solutions of various concentrations (0.05, 0.1, 1.0, and 3.0 wt %) were prepared and subsequently agitated and sonicated for 30 min for homogeneous dissolution. The 40-mL aqueous solutions then were placed in 100-mL cylinders. Unrefined pieces of cotton (10 mm × 10 mm) were dropped into the cylinders. The wetting power was determined by the measurement of the interval between the time at which a piece of cotton was placed in a cylinder and the moment at which it came into contact with the surface of the solution.

The emulsion stability was expressed as the volumetric ratio of the emulsified solution to the measured whole solution.²² An aqueous 1.0 wt % wetting agent solution (50 mL) and 10 g of a hydrophobic liquid, such as an organic solvent (toluene) or an animal oil (neat's-foot oil), were placed into a 100-mL measuring cylinder and agitated well for 2 min. The emulsion stability was then determined by the measurement of the separated height of the solution every 20 min with the following equation.¹⁶

$$\text{Emulsion stability} = 1 - \frac{h_s}{h_o} = \frac{h_e}{h_o} \quad (1)$$

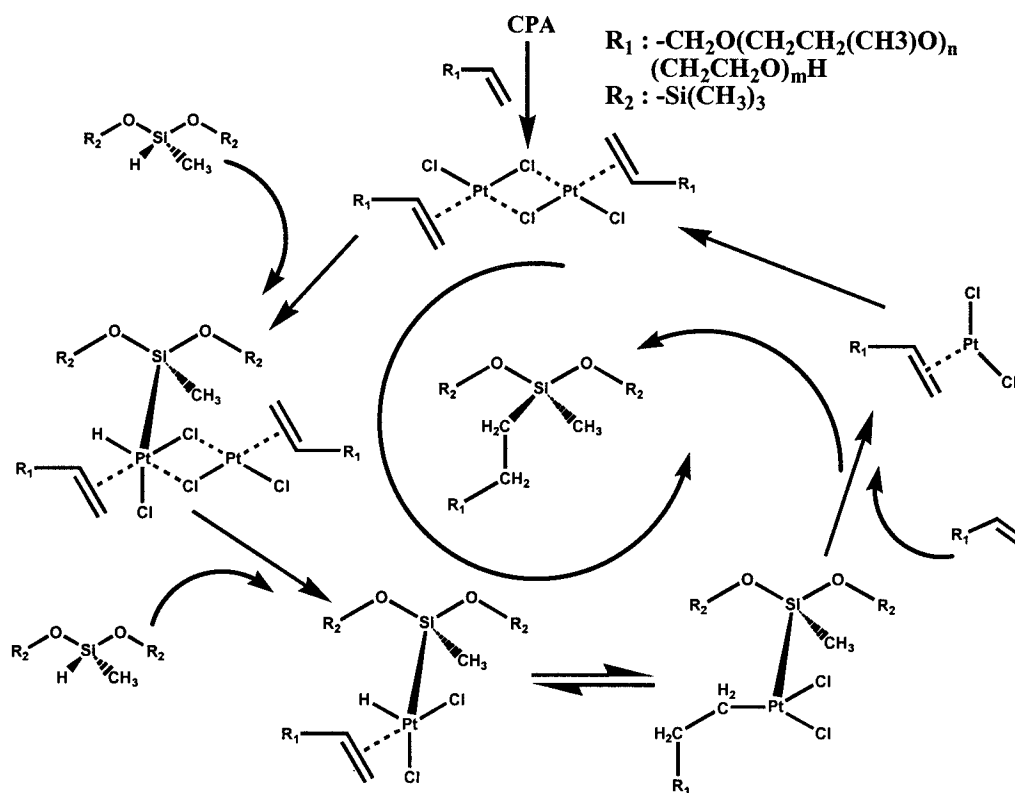
where h_s is the height of a separated solution, h_e is the height of an emulsified solution, and h_o is the height of a whole solution.

RESULTS AND DISCUSSION

Syntheses and characterizations

HMTS-oligo(PO-*b*-EO) was easily synthesized through the hydrosilylation of HMTS with active hydrogen and allyl oligo(PO-*b*-EO) with a platinum catalyst (Scheme 1). According to Chalk and Harrod's mechanism, the binuclear complex is formed through the reaction of an oxidative platinum catalyst and an organic compound with an unsaturated double bond. However, a Pt(IV) intermediate (π -bond complex) is formed through a reaction with siloxane with active hydrogen via a Pt(II) intermediate (σ -bond complex). As they turn into a binuclear complex with another compound, the hydrosilylation is completed.^{19,23–27}

Figure 1 shows FTIR spectra of HMTS-oligo(PO-*b*-EO) synthesized through the hydrosilylation of HMTS with active hydrogen and allyl oligo(PO-*b*-EO) with the CPA catalyst. The absorption bands at 2150 and 1660 cm⁻¹, corresponding to the unreacted Si—H stretching vibration peak of HMTS and the C=C stretching vibration peak of allyl oligo(PO-*b*-EO), were not observed for HMTS-oligo(PO-*b*-EO). Likewise, the completion of hydrosilylation was confirmed by the disappearance of these reactive groups.



Scheme 1 Synthetic route to HMTS-oligo(PO-*b*-EO) by hydrosilylation.

Figure 2 shows the $^1\text{H-NMR}$ spectrum of HMTS-oligo(PO-*b*-EO). The active hydrogen peak (Si-H) of HMTS at 4.6 ppm and the allyl group peak ($\text{CH}_2=\text{CH}-\text{CH}_2-$) of allyl oligo(PO-*b*-EO) at 5.2 and 5.9 ppm in HMTS-oligo(PO-*b*-EO) were not present. These results confirmed that HMTS-oligo(PO-*b*-EO)

was synthesized through hydrosilylation between the active hydrogen of HMTS and the allyl group of allyl oligo(PO-*b*-EO).

Figure 3 presents the molecular weights and molecular weight distributions for allyl oligo(PO-*b*-EO) as a reactant and HMTS-oligo(PO-*b*-EO) as a product with

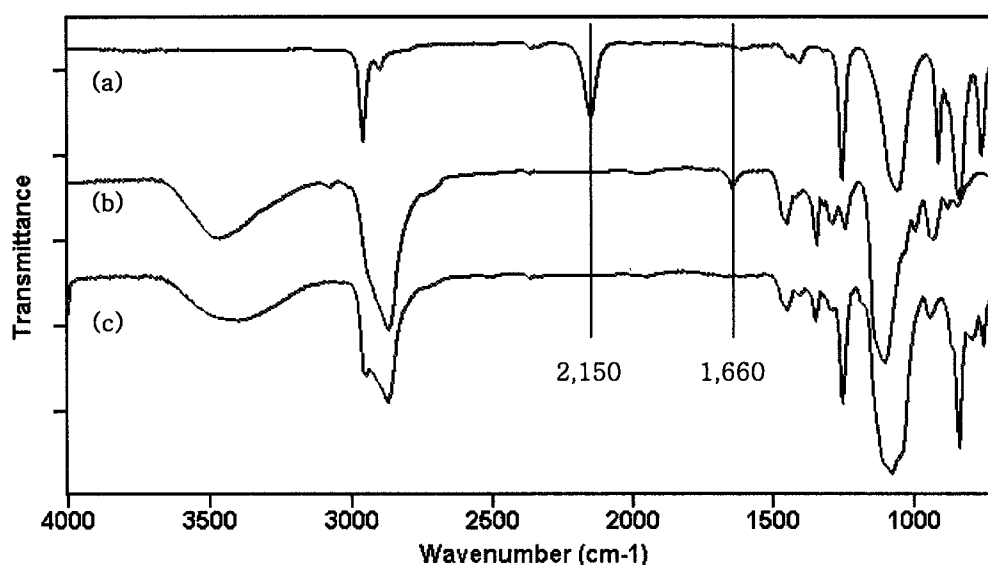


Figure 1 FTIR spectra of the reactant and the product from the hydrosilylation reaction: (a) HMTS, (b) allyl oligo(PO-*b*-EO), and HMTS-oligo(PO-*b*-EO).

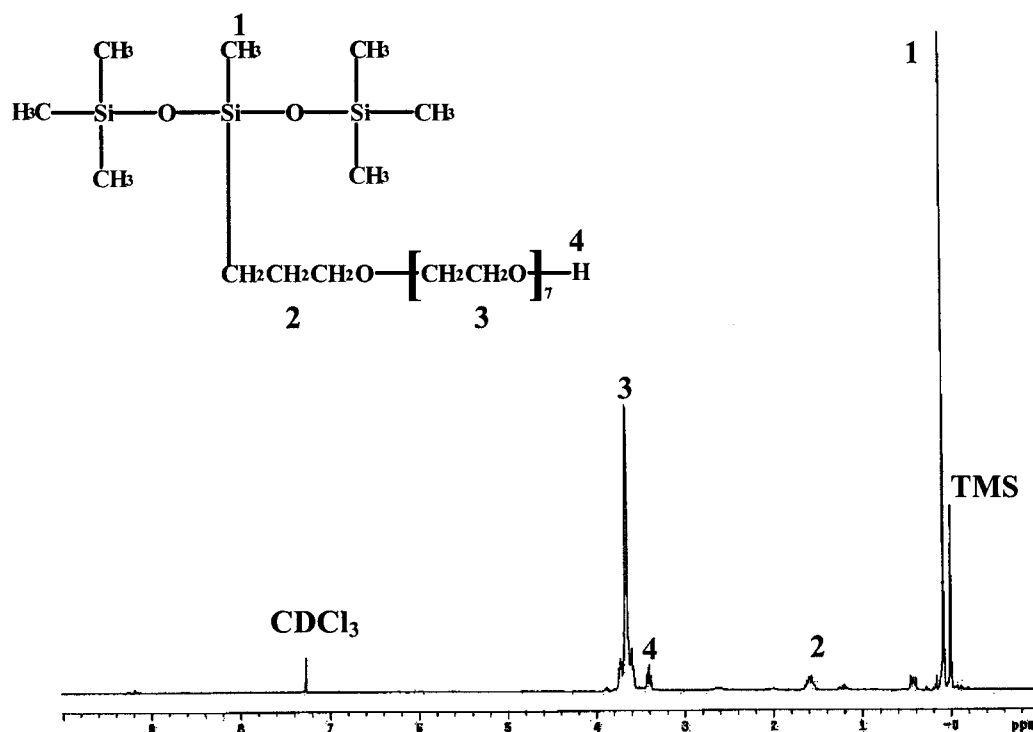


Figure 2 $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) spectrum of HMTS-oligo(PO-*b*-EO).

GPC chromatograms. The molecular weight of HMTS-oligo(PO-*b*-EO) was increased through hydrosilylation, and HMTS-oligo(PO-*b*-EO) had a molecular weight distribution similar to that of allyl oligo(PO-*b*-EO).

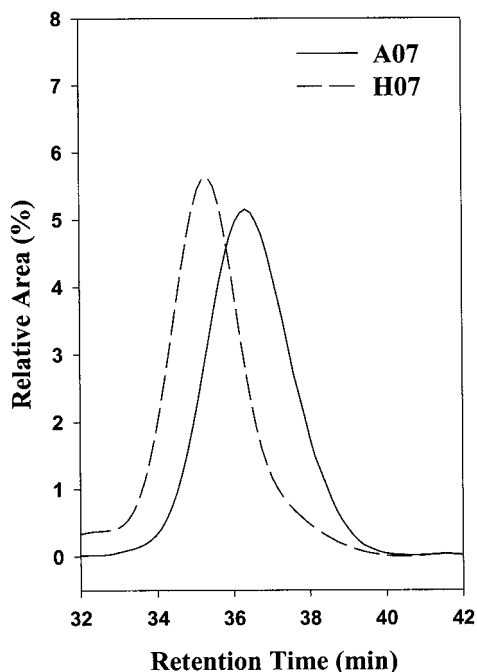


Figure 3 GPC chromatograms of allyl oligo(PO-*b*-EO) and HMTS-oligo(PO-*b*-EO).

Thermal properties

The weight-loss changes of allyl oligo(PO-*b*-EO) and HMTS-oligo(PO-*b*-EO) with increasing temperature were studied with TGA under nitrogen. The TGA measurements revealed that the thermal behavior was influenced by the chain length and EO/PO ratio of oligo(PO-*b*-EO).

Figure 4 shows the TGA curves of allyl oligo(PO-*b*-EO) and HMTS-oligo(PO-*b*-EO), which were used to observe the thermal behavior for hydrosilylation. The results showed that the initial weight-loss temperature of H07 and H34 was greater than that of A07 and A34. In particular, H07 showed a second weight-loss region of greater than 400°C, which was caused by hydrosilylation. Therefore, the weight-loss region of HMTS and PO was below 400°C. Likewise, the second weight-loss region of EO, which was stabilized by hydrosilylation, appeared above 400°C.

Figure 5 shows a weight-loss tendency for 1,1,1,3,5,5,5-heptamethyltrisiloxane-oligo(ethylene oxide) [HMTS-oligo(EO)] and HMTS-oligo(PO-*b*-EO) that depends on the chain length and EO/PO ratio of oligo(PO-*b*-EO). TGA in Figure 5(A) shows that the weight-loss temperature of HMTS-oligo(EO)s increased with an increased number of EO moieties. These two regions had a reduced weight loss at 300–400°C. The areas within the second weight-loss region above 300°C increased with an increased number of EO moieties in HMTS-

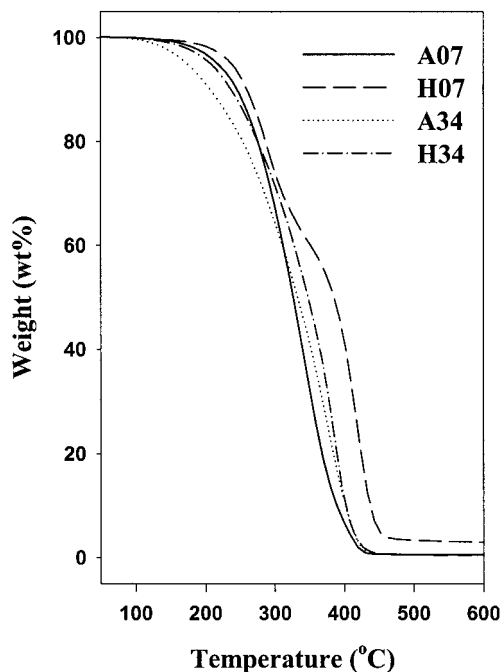


Figure 4 TGA thermograms showing changes in the weight loss with hydrosilylation.

oligo(EO), caused by stabilized oligo(ethylene oxide) [oligo(EO)]. Although the initial weight-loss temperatures for HMTS-oligo(PO-*b*-EO) were similar [Fig. 5(B)], two regions were presented as HMTS-

oligo(EO) [Fig. 5(A)]. As expected, the areas within the second region increased with increased EO and decreased PO. Accordingly, the second region occurred when EO moieties stabilized.

Lower critical solution temperature (LCST) behavior for the chain length and structure of hydrophilic moieties

Nonionic surfactants with hydrophilic and hydrophobic molecular parts can exhibit LCST behavior. The aqueous solutions of these surfactants exist as clear phases of hydrogen bonds with water below T_p . Above this temperature, the solutions exist as turbid phases separated between the surfactants and water. Likewise, hydrophobic-hydrophobic intermolecular interactions between surfactants exist as more than hydrogen bonds.^{3,4}

Table III indicates that HMTS-oligo(PO-*b*-EO) was almost visibly turbid at a 0.1 wt % concentration when synthesized through hydrosilylation with a hydrophobic group such as HMTS. A study on poly(siloxane ethoxylate) reported similar results.²⁸ Likewise, molecular HMTS was probably more hydrophobic than in other materials.²

Figure 6 shows the relative light intensity of HMTS-oligo(PO-*b*-EO) as the temperature increased with TOA for a 1.0 wt % aqueous solution. T_p was determined as the midpoint of the temperature in the phase transition through the extrapolation of the TOA ther-

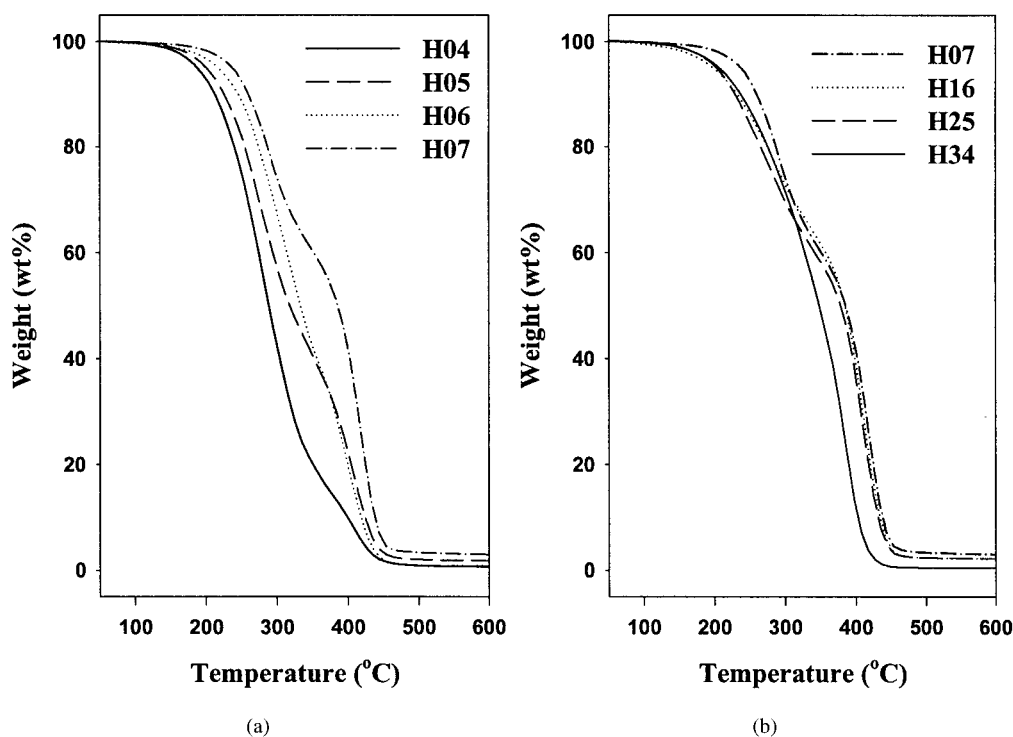


Figure 5 TGA thermograms of (A) HMTS-oligo(EO) and (B) HMTS-oligo(PO-*b*-EO) as a function of temperature.

TABLE III
Visible Turbidity of HMTS-Oligo(PO-*b*-EO)^a

Concentration (wt %)	HA04	HA05	HA06	HA07	HA16	HA25	HA34
0.01	T	NT	NT	NT	NT	T	T
0.1	T	T	T	T	T	T	T
1	T	T	T	T	T	T	T

^a T = turbid; NT = not turbid.

mogram. Figure 6(A) shows the phase-transition behavior of HMTS-oligo(EO) with a chain length of oligo(EO). For most of these solutions with an EO chain length of 4–7 mol, T_p was within the measured temperature range. T_p increased as the EO chain length increased. Hydrogen bonds between EO and water probably increased with increasing EO chain length. When these hydrogen bonds went beyond the interaction between hydrophobic groups such as HMTS, T_p also increased. HA04 with an EO chain length of 4 mol was below the measured temperature range because of the short EO chain length. Figure 6(B) shows the phase-transition behavior of HMTS-oligo(PO-*b*-EO) as the ratio of EO/PO with a chain length of 7 mol. T_p decreased with an increasing ratio of PO to oligo(PO-*b*-EO). However, the interactions between the hydrophobic groups increased with an increasing PO ratio. These interactions were more than hydrogen bonds at a lower temperature.

Table IV presents the T_p values for the wetting agent solutions.

Surface tension and cmc

According to the literature,^{2–6} the surface tension of an aqueous solution containing a siloxane wetting agent is less than that of a conventional surfactant because of the silicone existing in the hydrophobic part. It has also been suggested that these could form micelles with a lower concentration of the aqueous solution.

Figure 7 shows the surface tension with aqueous solutions of various concentrations for HMTS-oligo(EO) and HMTS-oligo(PO-*b*-EO). Overall solutions within the measured concentration range appeared at a lower surface tension below 40 dyn/cm. These were reduced with an increase in the concentration of the wetting agent for the aqueous solutions. Likewise, the surface tensions of these solutions de-

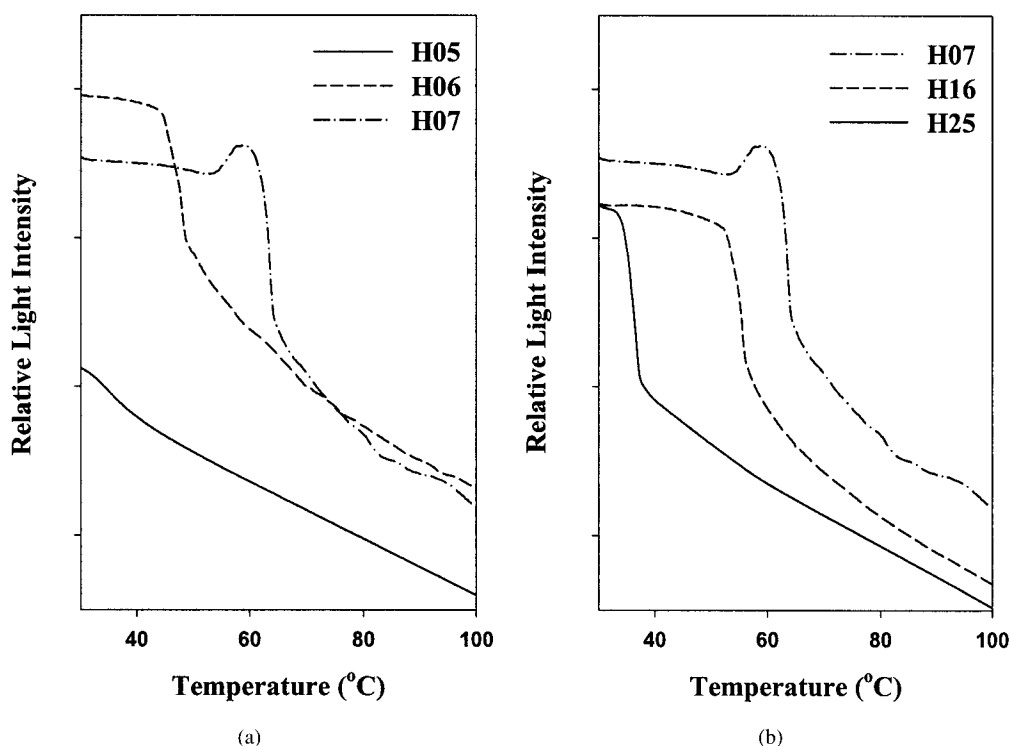


Figure 6 TOA thermograms of (A) HMTS-oligo(EO) and (B) HMTS-oligo(PO-*b*-EO).

TABLE IV
 T_p 's of HMTS-Oligo(EO) and HMTS-Oligo(PO-*b*-EO)

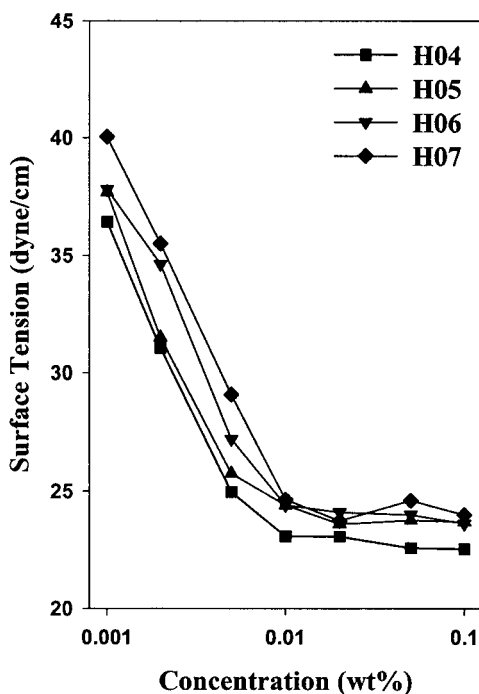
Sample	T_p (°C) ^a	Sample	T_p (°C)
HA04	— ^b	HA07	61.6
HA05	32.9	HA16	53.6
HA06	46.2	HA25	34.7
HA07	61.6	HA34	—

^a In an aqueous solution (1 wt %).

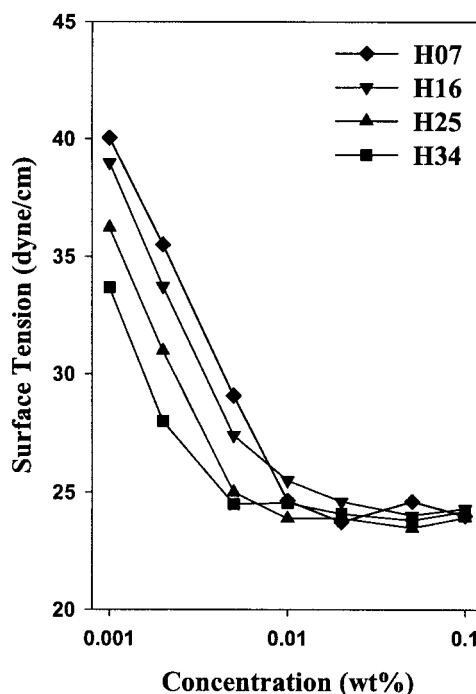
^b Not detected.

creased when concentration increased between 0.001 and 0.01 wt %, and they remained uniform above 0.01 wt %. As shown in Figure 7(A), the surface tensions with oligo(EO) as a hydrophilic group increased with an increased chain length of EO below cmc-formatted micelles similarly to others above cmc. The surface tensions probably decreased with increased EO chain length. Figure 7(B) shows the surface tensions for HMTS-oligo(PO-*b*-EO) with the same chain length of 7 mol but with various ratios of EO to PO. Similarly to Figure 7(A), Figure 7(B) shows that the surface tension was the same as the others above cmc but decreased considerably with an increased ratio of PO to oligo(PO-*b*-EO) as a hydrophobic group. This was due to an increased hydrophobic ratio (e.g., HMTS or PO as a surface tension reducer).

Figure 8 shows cmc for HMTS-oligo(PO-*b*-EO) with various chain lengths of EO and EO/PO ratios. The



(a)



(b)

Figure 7 Surface tension of (A) HMTS-oligo(EO) and (B) HMTS-oligo(PO-*b*-EO) as a function of concentration.

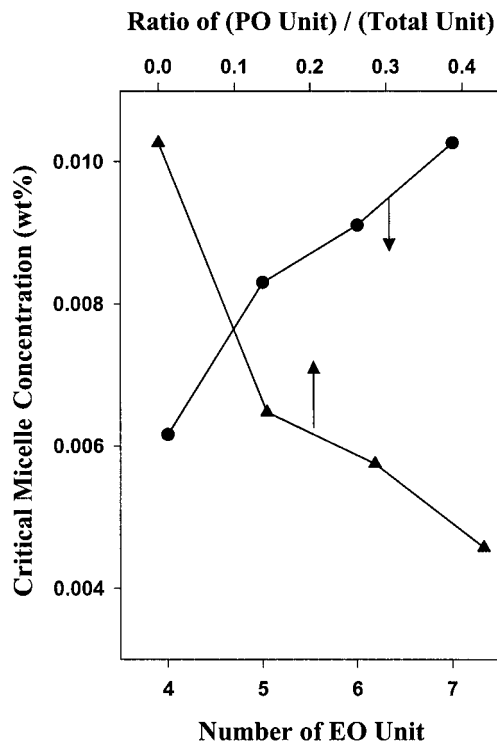


Figure 8 cmc of HMTS-oligo(PO-*b*-EO) as a function of the oligo(PO-*b*-EO) structure.

cmc's increased with the molecular EO chain length and decreased with the PO ratio for the same chain length of oligo(PO-*b*-EO). This was due to associated

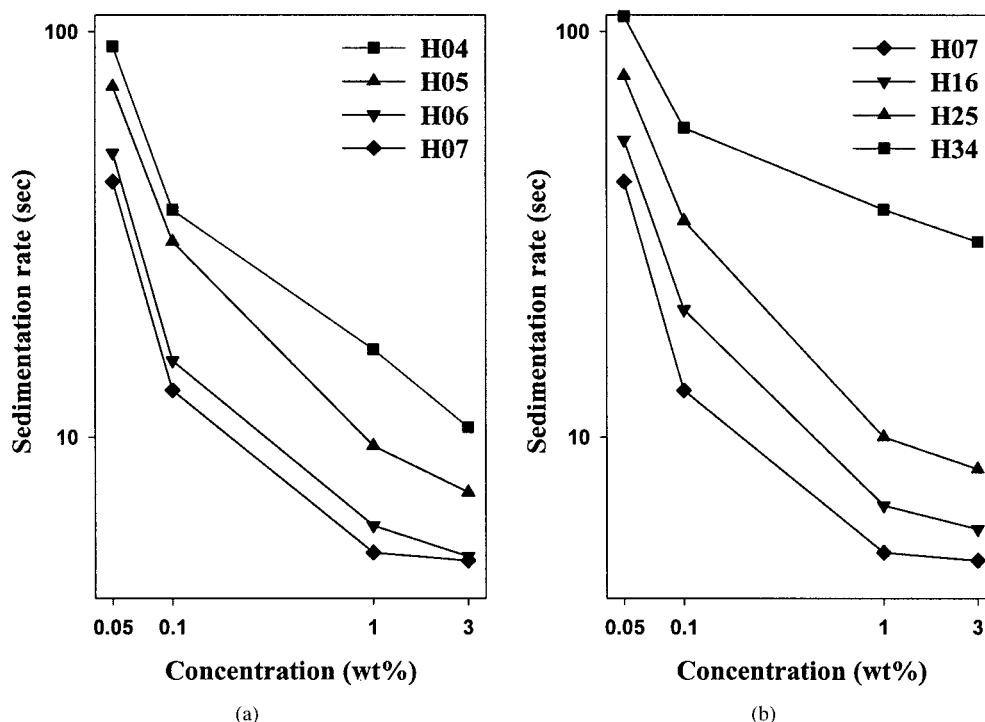


Figure 9 Wetting power of (A) HMTS-oligo(EO) and (B) HMTS-oligo(PO-*b*-EO).

micelles of a lower concentration with an increased hydrophobic ratio.

Wetting power

Figure 9 shows the wetting powers of HMTS-oligo(PO-*b*-EO) with various chain lengths and EO/PO ratios of oligo(PO-*b*-EO). When a hydrophobic cotton piece was soaked in an aqueous solution, with the wetting agent being capable of reducing remarkable interfacial tension, the wetting power for HMTS-oligo(PO-*b*-EO) could be determined as the sedimentation time following the absorption of the aqueous solution by the cotton piece.

When the overall aqueous solution was absorbed by the cotton piece, the wetting power increased with an increased concentration of the wetting agent used for the aqueous solution. Figure 9(A) shows the wetting power of HMTS-oligo(EO) with the EO chain length. The sedimentation time of the cotton piece decreased; it was kept uniform with increasing concentration. The wetting power of HMTS-oligo(EO) increased with an increase in the EO chain length of oligo(EO). However, this result was the reverse for increased surface tension. Generally, faster permeability increases the wetting power and reduces the surface tension. In contrast, the wetting power decreased in this study. As the EO chain length decreased, the wetting power increased with an increased hydrophobic ratio and decreased with the solubility of the wetting agent for

an aqueous solution. The wetting power probably decreased with decreasing molecular permeability as the solubility decreased. Figure 9(B) shows the wetting power of HMTS-oligo(PO-*b*-EO) with the EO/PO ratio. The wetting power of HMTS-oligo(PO-*b*-EO) increased with increased concentration and decreased when the PO ratio was used as a hydrophobic group. In this study, the wetting power was influenced more by solubility than by the surface tension.

Emulsion stability in two-phase systems such as oil in water

Siloxane wetting agents as nonionic surfactants can emulsify immiscible liquid phases between hydrophilic and hydrophobic liquids such as water and oil and can disperse one phase into another phase.^{29,30} Likewise, the structure of the surfactant can influence the stability of the emulsified solution. Figure 10 presents the emulsion stability for HMTS-oligo(PO-*b*-EO) in a toluene/water system. In this system, water existed as a continuous phase. The emulsion stability increased with increased EO chain length (EO being used as a hydrophilic group) and decreased with the PO ratio of oligo(PO-*b*-EO). When the emulsified toluene emerged as small droplets in the water, hydrophilic groups of surfactant molecules arranged on the water phase and stabilized the dispersed solution. Generally, the chain length of a hydrophilic group is more stable

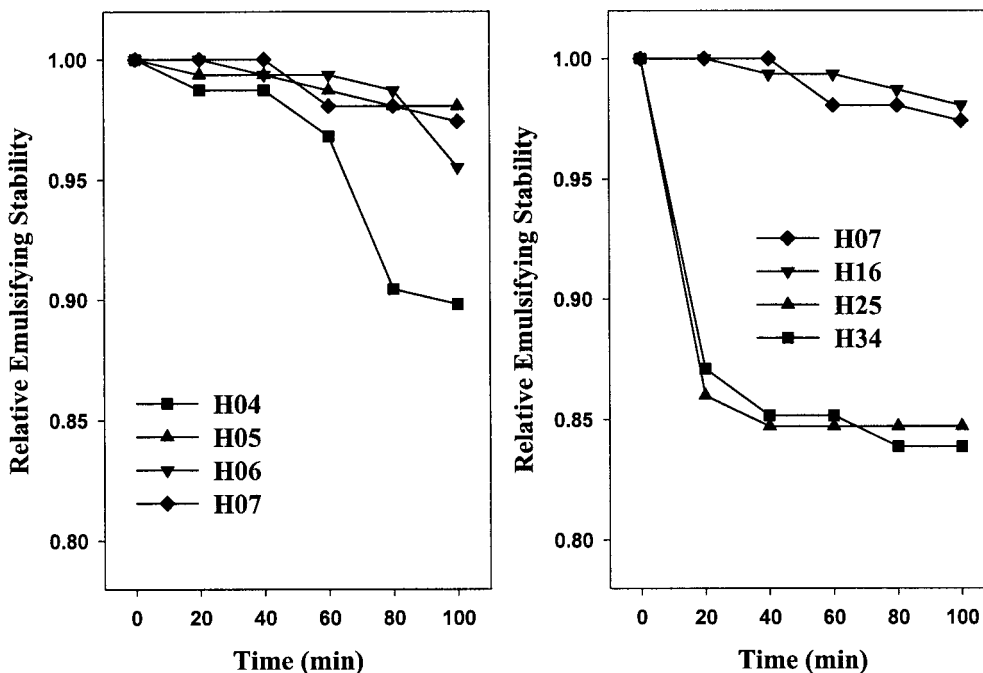


Figure 10 Emulsion stability of (A) HMTS-oligo(EO) and (B) HMTS-oligo(PO-*b*-EO) in the toluene-water system.

when a prolonged application of a surfactant with a larger hydrophilic ratio (> 10) is applied to emulsify an oil-in-water system.^{31,32}

Figure 11 presents the emulsion stability of HMTS-

oligo(PO-*b*-EO) in neat's-foot oil and water, which decreased in measurement and stability in comparison with the toluene and water system. This is because neat's-foot oil is more hydrophobic than toluene. It

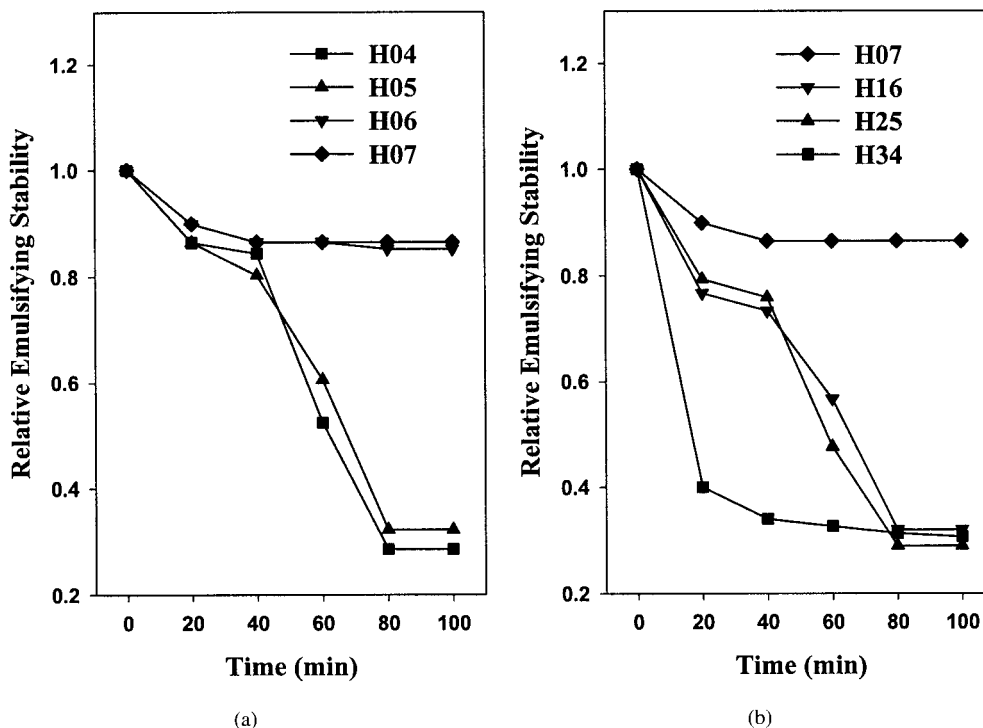


Figure 11 Emulsion stability of (A) HMTS-oligo(EO) and (B) HMTS-oligo(PO-*b*-EO) in the neat's-foot oil (animal oil)/water system.

also has a higher interfacial tension with water and requires a larger hydrophilic group.

CONCLUSIONS

In this study, HMTS-oligo(PO-*b*-EO) wetting agents were synthesized through hydrosilylation with HMTS as a hydrophobic group and allyl oligo(PO-*b*-EO) as a hydrophobic group with a platinum catalyst. Allyl oligo(PO-*b*-EO) with various hydrophilic–hydrophobic balances and chain lengths was synthesized to investigate the surface-active properties of HMTS-oligo(PO-*b*-EO). The purification and synthesis of the wetting agent were described. The following results were obtained from the measurement of the surface-active properties:

1. TGA of HMTS-oligo(PO-*b*-EO) revealed that the weight-loss temperature increased with an increased chain length and hydrophilic ratio of oligo(PO-*b*-EO). Areas with a second weight-loss region above 300°C increased with an increased EO ratio of oligo(PO-*b*-EO).
2. Wetting agent aqueous solutions with concentrations greater than 0.1 wt % were almost visibly turbid. They showed phase-transition behavior within the measured temperature range. Likewise, LCST showed a higher T_p with an increased number of hydrophilic groups of oligo(PO-*b*-EO).
3. As for the surface tension of dilute solutions, a lower surface tension of 20–25 dyn/cm was found within a concentration range of 0.01–0.1 wt %. The surface tension and cmc increased with an increased number of hydrophilic groups of oligo(PO-*b*-EO).
4. The wetting power increased with an increased concentration of the aqueous solution for whole samples. Likewise, a higher wetting power increased the number of hydrophilic groups of oligo(PO-*b*-EO), and this was probably due to the increasing solubility of the wetting agent for the aqueous solution.
5. As the emulsion stability at a 1.0 wt % concentration, better stability was exhibited with the hydrophilic group of oligo(PO-*b*-EO).

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